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THE INSECTICIDE FIPRONIL AND ITS DEGRADATES AS CONTRIBUTORS TO TOXICITY IN CENTRAL VALLEY SURFACE WATERS

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Background

Fipronil is an insecticide belonging to a class known as phenylpyrazoles. It was rarely used in California ten years ago, but is now emerging as an insecticide commonly used by professional pest controllers. Unlike many other insecticides, the compound is not registered in California for any agriculture use. It is used nearly entirely for structural pest control and landscape maintenance, and thus its presence in surface waters would be expected to be of urban origin. While originally used for termite control, several years ago it was approved for treatment of ants, an above-ground application that would make residues susceptible to off-site movement to surface waters.

Fipronil can be quite toxic to aquatic life, with LC_{50}s to many aquatic invertebrates in the low µg/L, and the most sensitive reported being the mysid shrimp with an acute EC_{50} of 140 ng/L and full life-cycle effects on survival reproduction and growth at less than 5 ng/L (EPA, 1996). However, what makes ecotoxicology of the compound so challenging is that fipronil has a variety of environmental degradates. The major photodegradation product is fipronil desulfinyl. Oxidation creates fipronil sulfone, reductive processes produce fipronil sulfide, and hydrolysis yields fipronil amide. Many of the environmental degradates are even more toxic than the parent compound.

Fipronil is moderately hydrophobic, with a log K_{oc} of about 3, thus it can be expected to be found in both sediment and water. Except for the very water-soluble amide, the other degradates are all somewhat more hydrophobic than the parent compound. Once adsorbed to particles, fipronil and its degradates are relatively persistent. Reported fipronil sediment half-lives are commonly 0.5-3 months, and the degradates are even more persistent, with the sediment half-lives of approximately 1-2 years (Lin et al., 2008; 2009; Brennan et al., 2009).

Problem Statement

Recent monitoring of urban runoff by the Department of Pesticide Regulation (DPR) found fipronil or its degradates in many urban runoff samples analyzed. In sampling creeks around Sacramento and the San Francisco Bay areas (Ensminger and Kelley, 2011a), 84% of the samples contained fipronil, 21% above the reporting limit (50 ng/L). Five percent of the samples had concentrations exceeding the value DPR employed as a benchmark for acute toxicity (110 ng/L). Many more samples exceeded the chronic toxicity benchmark (11 ng/L), but could only be reported as “trace concentrations” since the chronic toxicity benchmark is well below DPR’s reporting limit of 50 ng/L. A recent CALFED-funded study also commonly found fipronil and/or its degradates. Fipronil was detected in 66-85% of samples in the Sacramento area, though was only occasionally expected to be toxic. In Orange County, where concentrations were considerably higher, even the median concentration exceeded toxicity thresholds for sensitive species (Gan et al., 2012). We also note that when Gan conducted this work (2006-2008) and reported much higher fipronil concentrations in Orange County than in Sacramento County, use of the compound in Orange County was greater by six fold. However, by 2010 (most recent available data), Orange County fipronil use had declined and Sacramento County's had increased, leading to only a three-fold difference currently.

Yet the scope of the problem cannot be well defined with existing data. Monitoring has been very limited, and nearly all of what has been done has been sampling directly from storm drains. Surface water monitoring has been limited to DPR sampling (Ensminger and Kelley, 2011a: 2011b) of eight creeks or rivers scattered throughout California. Specifically within Region 5, the only creeks with surface water data for fipronil and degradates are Pleasant Grove Creek in Roseville and Alder/Willow Creeks in Folsom. Interpretation of existing chemical data is complicated by the fact that LC_{50} data are available for only a small number of species, and are lacking for some key species commonly used for toxicity testing (e.g., no water LC_{50} data for Chironomus dilutus, no sediment or water LC_{50} data for Hyalella azteca). Toxicity data on fipronil degradates is extremely limited. In short, fipronil is an emerging pesticide in California with minimal monitoring data, and little toxicological data. Existing data are sufficient to indicate the potential for environmental harm, but are insufficient to establish the magnitude of the threat.

Target Audience and Management Decisions

Work in recent years has demonstrated that insecticide use in urban environments can adversely affect water quality in receiving waters. The magnitude of use of many insecticides in urban systems can surpass those used in California agriculture, and the protection of urban aquatic systems from pesticide runoff is particularly challenging with the limited information and fewer regulatory tools available in urban settings (no reporting of retail sales data in the Pesticide Use Reporting database, no licensing of the homeowners who apply pesticides, harder to identify responsible parties, and quite likely less adherence to label instructions by homeowners).

The planned work is specifically intended to assist Water Board staff in assessing the risk from an emerging pesticide for which little environmental monitoring has been done. It is conceived as a screening level study that will help establish whether more focused studies are necessary, and whether fipronil and its degradates should be incorporated into on-going monitoring programs. The information gained from this project will also assist Water Board staff in reporting for 305(b) requirements as well as in determinations of whether water bodies should be placed on the 303(d) impairment list, and if stressor identification and load allocation assessments for total maximum daily load (TMDL) development are necessary.

The DPR will also benefit from this study. Evaluating urban pesticide use is a high priority for DPR, and the data gathered will aid management decisions regarding pesticides used in urban systems, and their methods of application by professional pest controllers and homeowners.

Assessment Question

Information to support management decisions can be obtained by answering the following assessment question: Is fipronil or some of its most common environmental degradates present in concentrations that could be a threat to aquatic life in urban surface waters within the jurisdiction of the Central Valley Regional Water Quality Control Board, Sacramento office (roughly, Central Valley from Yuba City to Modesto, and hereafter referred to as Region 5S)?

Monitoring Goal

The goal of the current study is to provide monitoring data on fipronil, its degradates, and any associated toxicity in surface water bodies throughout Region 5S that receive substantial amounts of urban runoff. Though not the primary objective of this project, the planned sampling will also provide useful data on pyrethroid insecticides in urban runoff, assisting on-going surface water protection efforts related to this compound class.

Linkage to Beneficial Uses

Region 5S water bodies provide habitat for aquatic ecosystems that include benthic and water column invertebrates, which form important links in food webs supporting many native fish species. This study focuses on potential impacts to these aquatic invertebrate communities and the ecosystems they support.

Spatial Scale

All sampling will occur in Region 5S. Sampling will occur throughout that portion of the Valley bounded by Yuba City to the north, and Stockton to the south.

Temporal Scale

Samples will most likely be collected over slightly more than a year. The majority of wet season sampling will occur in the winter of 2011/2012, but may continue into the winter of 2012/2013 if needed. Dry season samples will be collected in the summer of 2012.

Indicators and Measurement Parameters

The chemical indicators used will primarily be analyses of whole, unfiltered water samples collected just below the surface. Chemical analytes will consist of fipronil, fipronil sulfide, fipronil sulfone, fipronil desulfinyl, and eight commonly used pyrethroid pesticides (bifenthrin, cyfluthrin, cypermethrin, esfenvalerate, lambda-cyhalothrin, deltamethrin, fenpropathrin, and permethrin). The whole-water samples will be extracted by liquid:liquid extraction using dicloromethane, and then analyzed by gas chromatography with electron capture detection. Six sediment samples will also be analyzed for fipronil and its degradates. We have published details on the analytical methods in Brennan et al. (2009), You et al., (2008), and Wang et al. (2009).

Toxicity testing will consist of 96-h acute tests of water samples using Hyalella azteca and Chironomus dilutus. H. azteca test endpoints will include mortality and paralysis. While there are no standard, nationally-adopted protocols for water testing with H. azteca, the species is used for this purpose in several California laboratories, and there are many publications describing this use (e.g., Werner et al., 2010; Weston and Lydy, 2010, and others).

Similarly, C. dilutus has no standard method for its use in water testing, but several publications have described a method for this purpose (e.g., Belden and Lydy, 2000, and others). Briefly, C. dilutus are held for 96 hours in water, with a thin layer of clean silica sand on the bottom to help avoid cannibalistic interactions. At test completion, C. dilutus are evaluated for their ability to execute the typical figure-8 swimming behavior when prodded, since some toxicants, particular neurotoxic pesticides, cause paralysis but not death within the duration of the test.

Sampling is expected to yield about 36 water samples for chemical analysis and toxicity testing (not counting QA samples, full details for which can be found in this project's Quality Assurance Project Plan), and approximately six sediment samples for chemical analysis. Nominal reporting limits in water samples are anticipated to be 3 ng/L, though we are usually able to report to 1 ng/L provided there are no unexpected matrix interferences. Reporting limits for sediment are expected to be 1 ng/g.

All pesticide chemical analyses will be conducted by Dr. Michael Lydy at the Fisheries and Illinois Aquaculture Center, Department of Zoology, Southern Illinois University using SWAMP-comparable methods. Toxicity testing will be conducted by Dr. Donald Weston at the University of California, Berkeley.

Monitoring Objectives

Existing data are extremely limited, making it impossible to know the environmental risks posed by the use of fipronil. Therefore, this study is designed to provide screening-level data to establish if more detailed investigations are warranted, and if so, to provide guidance on the types of water bodies at greatest risk and the toxicity testing tools best suited for this emerging compound.

The planned work is being leveraged with a concurrent study, funded by the Delta Science Program, that will establish LC_{50} thresholds of fipronil and its degradates for several aquatic species (among them the species used for testing in the planned work), and thereby aid interpretation of the chemical data gathered through this SRWCB-funded study.

Monitoring Design

As there are no approved agricultural uses of fipronil in California, sampling will focus largely on water bodies carrying runoff from urban areas. A tentative list of potential sampling sites is provided below, though minor adjustments may occur as the work progresses. The location of sites is shown in Figure 1.

Vacaville

1. Ulatis Creek at Leisure Town Rd.
2. New Alamo Creek at Meridian Rd.

Woodland

3. Willow Slough Bypass at County Rd. 102

Sacramento

4. Chicken Ranch/Strong Ranch Sloughs at American River confluence
5. American River at Highway 160 (Camp Pollock)

6. Arcade Creek at Rio Linda Blvd.

Florin

7. Morrison Creek at Shining Star Dr.(near Franklin Blvd.)

Carmichael

8. Carmichael Creek at Palm Dr.

Rancho Cordova

9. Buffalo Creek at American River confluence

Folsom

10. Hinkle Creek at Cascade Falls Dr.

Roseville

11. Pleasant Grove Creek at Fiddyment Rd.

12. Kaseberg Creek at Timberrose Way

Stockton

13. Mosher Slough at Mariner's Dr.

14. Smith Canal at Ryde Ave.

Yuba City

15. Gilsizer Slough at Lincoln Rd.

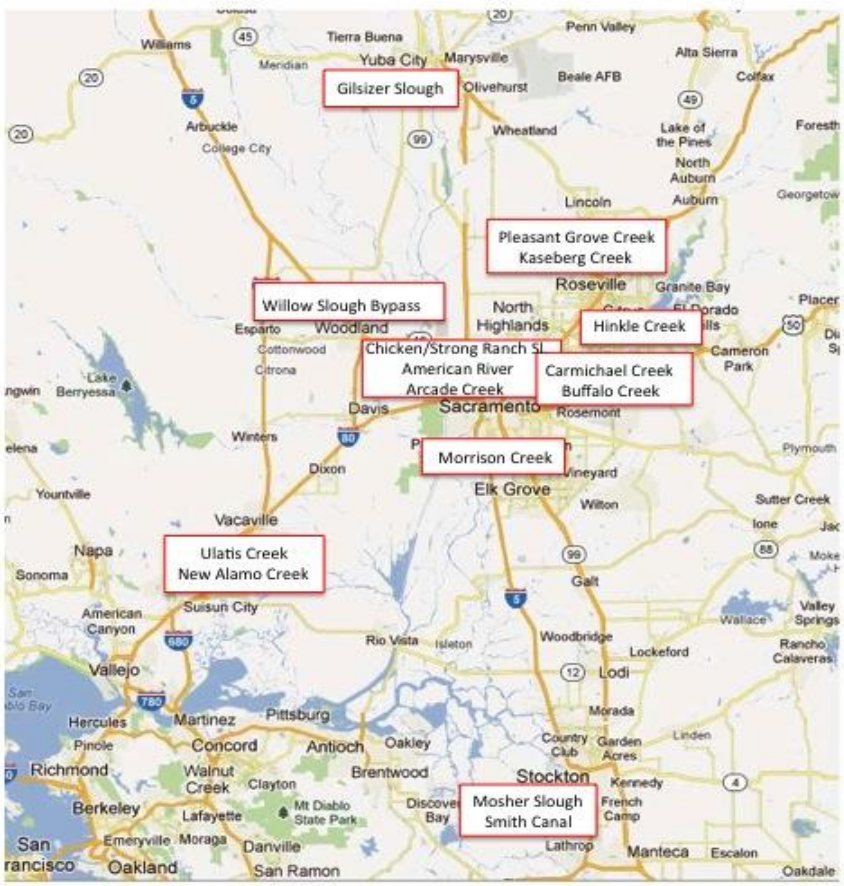

Figure 1. Planned sampling sites.

Sampling will occur in both the wet and dry seasons, and both will include a primary and secondary sampling round. Wet season sampling will be rain-triggered. All or nearly all of the sites listed above will be sampled in the primary round during a stormwater runoff event (though not necessarily the same event at all 15 sites). Runoff will be characterized by a single grab sample, if possible taken soon after 0.5 inches of rain in a given event has fallen. While we recognize that characterization of runoff quality could be done more precisely by composite sampling throughout the hydrograph, the large number of sites and the considerable distances separating them preclude this approach because of logistical considerations. Moreover, the study is only for screening purposes to obtain information on the range of fipronil and degradate concentrations found in surface water of Region 5S, and not to provide temporally intensive investigation of specific sites. The later approach may prove warranted at select sites after reviewing the data of the present study.

Water samples collected during the primary round will be used for chemical analysis of fipronil and pyrethroids, as well as toxicity testing with H. azteca and C. dilutus. Those sites with the highest concentrations of fipronil and degradates, tentatively assumed as three sites, will be resampled in a secondary round, following a subsequent rain event, in order to determine if the same sites having relatively high concentrations persist with repeat sampling. This secondary round will resample water for chemical analysis and toxicity testing as in the first round, but will also include a sediment sample for analysis of fipronil and degradates. As fipronil and degradates are moderately hydrophobic, they are likely to be in the sediment as well as in the water column, and this design will provide data on both matrices for the most problematic sites, but water-only data at sites with little fipronil in the water column.

The dry season sampling will follow the same basic approach, with a primary round at all sites, and a secondary round at a few sites with the highest concentrations as discovered in the primary sampling. Sampling will be done at least a week after any rain event. Our previous work with urban runoff has demonstrated peak runoff flow from residential irrigation occurs between about 5 AM and 10 AM (Weston et al., 2009). We will endeavor to sample during this period at most urban creek sites, to the extent that logistics and daylight permits. Assuming three sites for secondary round sampling in both the wet and dry season, the entire project will yield:

- 36 water samples for analysis of fipronil and degradates.
- 36 water samples for analysis of pyrethroids.
- 36 total suspended sediment samples, concurrent with pesticide sampling.
- 6 sediment samples for analysis of fipronil and degradates.
- 6 sediment total organic carbon samples, concurrent with the fipronil sampling.
- 36 water samples for testing with H. azteca.
- 36 water samples for testing with C. dilutus.

Field duplicates and other QA samples not included in the above totals.

Both H. azteca and C. dilutus are standard species for toxicity testing of freshwater sediments, but both have proven to be suitable for water-only tests as well, a valuable attribute for a compound such as fipronil which could be present at toxic concentrations in either matrix. There are no published LC_{50} data for fipronil and degradates in water for either of the species, but we are now generating these under our concurrent Delta Science Program project noted above. Sediment LC_{50} data for fipronil and degradates have been published for C. dilutus by the Lydy lab (Maul et al., 2008), and a student in the Weston lab has generated unpublished fipronil sediment LC_{50} data for H. azteca. These data suggest C. dilutus is about two orders of magnitude more sensitive to fipronil than is H. azteca, thus leading to our choice to include it in the current study despite the fact that it is not widely used in California monitoring.

It is already well established that pyrethroids are likely to be present at many of the sites to be sampled. They will quite likely be in sufficient concentrations to cause toxicity to H. azteca, and potentially C. dilutus, in some of the worst instances. Pyrethroids, therefore have been included among the intended analytes, though they are not the primary focus of this study, but the data will be necessary to help establish the cause of toxicity should it be observed. The two-species testing approach should also be helpful in this regard, since we would expect greater toxicity to H. azteca if pyrethroids are responsible, but greater toxicity to C. dilutus if caused by fipronil. Should toxicity be observed, we will also have LC50 data for both species and all compounds of interest, in order to determine if concentrations are high enough to explain the effects of observed (i.e., toxic unit analysis).

Coordination and Review Strategy

To promote monitoring coordination among agencies and work groups, this study will be reviewed/coordinated on multiple levels. First, there will be close coordination with Water Board staff in Region 5S. Second, the Contaminants Work Team (CWT) will be kept informed of study findings and given opportunities for suggestions and comments. This will primarily be done through the periodic meetings of the CWT at which one or more oral presentations on the study will be provided.

Finally, it is our practice to publish our work in the peer-reviewed literature, and we expect this will be the case with this study as well. Peer review, coordinated by the journal's editor, will insure the work meets or exceeds generally accepted standards of scientific rigor.

Quality Assurance

A project specific Quality Assurance Project Plan (QAPP) will be prepared that is consistent with the EPA 24 Element QAPP Guidelines and the SWAMP Quality Assurance Management Plan. The QAPP will include criteria for data acceptability, procedures for sampling, testing, and calibration, as well as preventative and corrective measures.

Data Management

All data generated by this project will be maintained as described in the SWAMP-accepted project QAPP. UCB staff will be responsible for collection of samples and field data and for entering the field data into the SWAMP database. Southern Illinois University (SIU) will be responsible for providing analytical chemistry data in SWAMP format.

Assessment Benchmarks

There are no enforceable threshold concentrations or Basin Plan Objectives for fipronil in water. Under a project funded by the Delta Science Program, we are developing water LC_{50}s for fipronil and its degradates using H. azteca, C. dilutus, and a variety of local, wild-caught benthic macroinvertebrates. Fipronil data gathered under the current study will be evaluated on the basis of these emerging toxicity data, the limited water data that exist in the literature, and fipronil sediment toxicity thresholds for C. dilutus.

For pyrethroids in water, UC Davis, under contract to the Central Valley Water Board, has reviewed all available toxicity data for a few pyrethroids, and derived acute and chronic thresholds for protection of aquatic life. Their bifenthrin thresholds have been incorporated in an on-going TMDL in southern California. The data gathered in the planned study can be compared against these thresholds for bifenthrin, cyfluthrin, and lambda-cyhalothrin. In addition, we have published water LC_{50} data for H. azteca exposed to a variety of pyrethroids (Weston and Jackson, 2009), and these data will be helpful in interpreting toxicity testing results.

Reporting

Data collected from this assessment will be transferred to, and be electronically available from, the SWAMP database. A final project report, probably in the form of a publishable paper, will be prepared.

Project Schedule

Activity	Date
Draft Monitoring Plan (MP)	November 2011
Draft Quality Assurance Project Plan (QAPP)	December 2011
Final MP and QAPP	March 2012
Sample Collection	Winter 2011/2012, summer 2012, and winter 2012/2013 if needed
Reporting Draft Final Report Final Report	 May 2013 June 2013
Expected Project Completion Date	June 2013

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